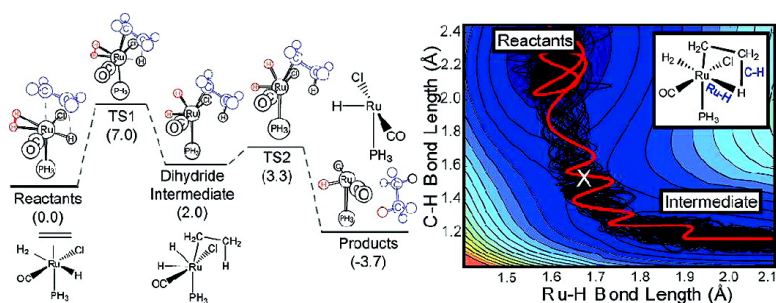


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*J. Am. Chem. Soc.*, **2008**, 130 (23), 7218-7219 • DOI: 10.1021/ja802219a • Publication Date (Web): 16 May 2008

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A Path Sampling Study of Ru-Hydride-Catalyzed H<sub>2</sub> Hydrogenation of Ethylene

Christopher N. Rowley and Tom K. Woo\*

Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie-Curie, Ottawa, ON, K1N 6N5 Canada

Received March 25, 2008; E-mail: twoo@uottawa.ca

Computational chemistry has made many important contributions to the study of reaction mechanisms in organometallic chemistry, allowing short-lived intermediate and transition states structures of a reaction mechanism to be located and analyzed.<sup>1</sup> Although computational chemistry has successfully modeled aspects of chemical reactivity, most studies only identify potential energy minima (reactants, products, and intermediates) and saddle points (transition states). Even at moderate temperatures, vibrational effects can be essential to the full understanding of a reaction mechanism.<sup>2</sup> The range of thermally accessible structures, the intense molecular vibrations involved in crossing transition states, and the redistribution of vibrational energy in reaction intermediates are important features of a mechanism but are unobtainable from the potential energy reaction profile alone. Simulating the motion of the atoms through time with ab initio molecular dynamics (MD) simulations is a powerful means to examine these effects;<sup>3</sup> however, reactions with significant barriers, such as those present in many organometallic reactions, need impractically long simulations to be observed.

Commonly, this time scale problem is circumvented by imposing artificial forces to drive the system across the reaction coordinate in a short simulation. While this approach has yielded many significant insights in a range of catalytic systems,<sup>4</sup> the true dynamics of the reaction are masked by these artificial forces. One promising technique for addressing this problem is transition path sampling, an innovative Monte Carlo scheme that allows reactive events, such as chemical reactions, to be studied with MD.<sup>5</sup> Given an initial trajectory,<sup>6</sup> path sampling can generate an ensemble of reactive, dynamical trajectories. This ensemble can then be analyzed to describe the dynamics of the reaction. Recent transition path sampling studies have explored biomolecular isomerization,<sup>7</sup> enzymatic reactions,<sup>8</sup> and reactions in solution.<sup>9</sup> Although the MD simulations used in these studies neglect quantum effects, such as vibrational energy quantization and tunneling,<sup>3</sup> these simulations still serve as an approximate means to examine the dynamical features of chemical reactions.

Combined with density functional theory (DFT), path sampling has great potential for investigating organometallic reactions. In this study, we have used MD in conjunction with path sampling to examine the dynamics of key steps in a notable catalytic reaction: the H<sub>2</sub> hydrogenation of ethylene with the catalyst RuHCl(CO)(PR<sub>3</sub>)<sub>2</sub>, a mainstay of homogeneous catalysis.<sup>10</sup> The calculated potential energy surface of the insertion and elimination steps, not including zero-point corrections, is summarized in Figure 1.<sup>11</sup> The critical step of this mechanism is the insertion of ethylene into the Ru–H bond (TS1), which leads to a dihydride intermediate that undergoes reductive elimination of ethane through a 1.3 kcal mol<sup>-1</sup> barrier (TS2). This is an exemplary subject for a path sampling study, as it involves three important reaction steps: olefin insertion into an M–H bond, oxidative addition of H<sub>2</sub>, and a reductive elimination. While our DFT calculations predicted that the intermediate was unambiguously Ru(IV), previous

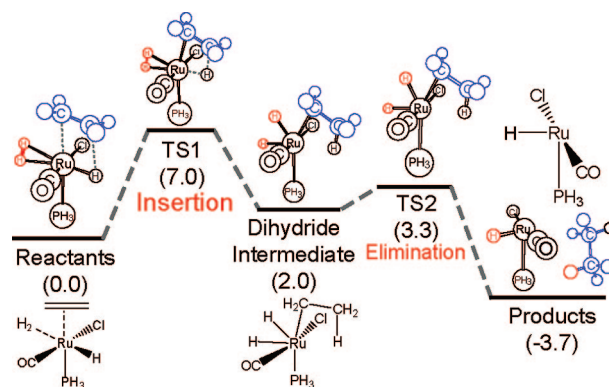


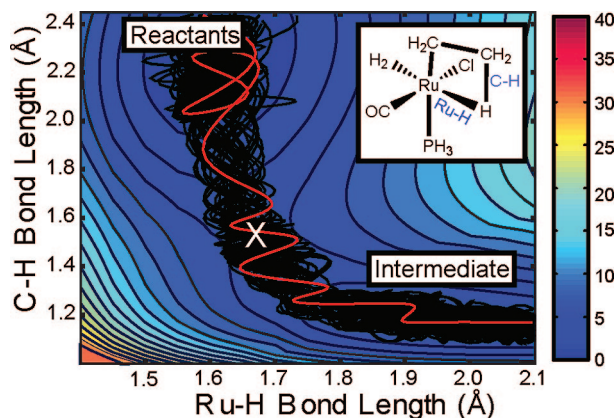
Figure 1. Potential energy reaction profile for the insertion (TS1) and elimination (TS2) steps. Energies in parentheses are in kcal mol<sup>-1</sup>.

reports had precluded this possibility, as nonclassical Ru(II)–H<sub>2</sub> complexes are more commonly observed experimentally.<sup>12</sup> Herein, we report an MD and path sampling study of the insertion and elimination steps of this catalytic cycle to analyze the dynamics of these reaction steps and resolve the nature of this surprising Ru(IV) dihydride intermediate.<sup>13</sup>

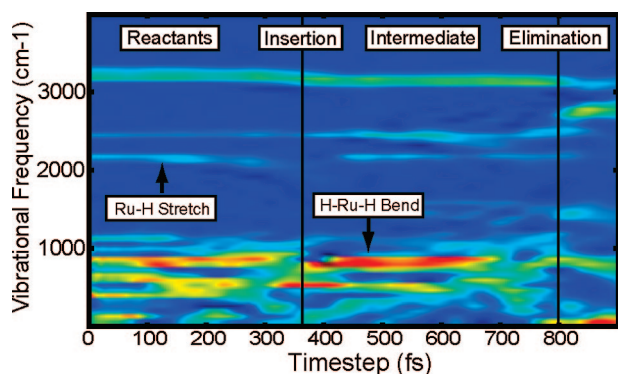
First, to examine the reactant structure at room temperature, a 20 ps molecular dynamics simulation was run. While nonclassical effects will be significant for the dynamics of the coordinated H<sub>2</sub>, we can infer from these simulations that the H<sub>2</sub> has a large degree of configurational freedom, with large fluctuations in the Ru– $\eta^2$ (H<sub>2</sub>) distance (the rmsd of the Ru– $\eta^2$ (H<sub>2</sub>) distance is 0.12 Å). Conversely, the Ru– $\eta^2$ (C<sub>2</sub>H<sub>4</sub>) distance fluctuates in a much smaller range, with an rmsd of 0.05 Å and the C–C axis of the ethylene remains close to its minimum energy orientation, eclipsing the Ru–H bond, with an rmsd of the hydride–Ru–C=C dihedral angle of 11°. This is consistent with the stronger coordination of the ethylene to the metal (32.2 kcal mol<sup>-1</sup>) compared to H<sub>2</sub> (7.2 kcal mol<sup>-1</sup>).

We then examined the ethylene insertion process using path sampling: 150 reactive trajectories where ethylene insertion occurs were harvested. A typical trajectory shows localization of kinetic energy into the Ru–H stretching and bending modes prior to insertion, followed by alignment of the ethylene over the Ru–H bond. Simultaneously, the hydride is transferred to the ethylene and the coordinated dihydrogen cleaves, forming the intermediate. The C–H bond formed in this step immediately forms an agostic interaction with the metal. The TS1 barrier can be crossed (C–H = 1.58 Å in Figure 2) at a variety of Ru–H bond lengths; trajectories crossed the transition state with Ru–H distances that ranged between 1.65 and 1.75 Å. This reflects that the Ru–H bond is vibrationally excited during the insertion.

After crossing TS1, only the 1.3 kcal mol<sup>-1</sup> TS2 must be crossed to eliminate ethane, a common motif in reaction mechanisms, where a large, rate-limiting barrier precedes a small barrier. The ubiquitous



**Figure 2.** Reactive trajectories on the PES of the insertion (TS1). The indicated ruthenium–hydride bond and carbon–hydrogen bonds are used. The white X indicates the location of the potential energy transition state. The trajectory analyzed in Figure 3 is shown in red. Energies are in kcal mol<sup>-1</sup>, relative to the optimized reactants.



**Figure 3.** Vibrational spectrogram of a trajectory with a dihydride lifetime of 400 fs. Red and blue areas indicate high and low intensity, respectively.

RRKM model has significant shortcomings for estimating the lifetime of this intervening intermediate because it relies on the harmonic approximation to represent vibrational modes, despite significant anharmonicity, and assumes an equilibrium distribution of kinetic energy in the reaction intermediate, which may not be realistic following a reaction step where kinetic energy has been localized in specific vibrational modes.<sup>14</sup>

Path sampling is a promising means to examine intrinsic non-RRKM effects in chemical reactions. The trajectories harvested provide a range of vibrational energy distributions that reflect the localization of kinetic energy in the newly formed intermediate and the harmonic approximation is not necessary. We have extended the trajectories crossing TS1 that we harvested forward in time until the simulation crossed TS2. Of the 150 trajectories sampled, 21 recrossed TS1 to revert to the reactants rather than undergoing elimination. Almost 70% of the remaining trajectories crossed TS2 within 1 ps of the formation of the intermediate, and all trajectories underwent elimination within 3 ps.<sup>15</sup> In contrast, the RRKM model predicts a half-life of 8 ps. This rapid decay indicates that the localization of kinetic energy in the intermediate causes TS2 to be crossed quickly.

To understand this exceptionally short half-life, we have calculated the vibrational spectrogram<sup>16</sup> of a representative trajectory to show the redistribution of kinetic energy in vibrational modes over the course of the reaction (Figure 3). Ru–H stretching and bending vibrations are notably excited prior to the insertion. After the insertion, the hydrides formed by cleavage of the coordinated H<sub>2</sub> gain vibrational energy. Starting near 700 fs, the intermediate

undergoes a fluctuation where the dihydride H–H distance contracts to 0.94 Å, transiently forming a nonclassical dihydride structure. This is consistent with the disappearance of the H–Ru–H bending modes starting at 700 fs in Figure 3. A H–H stretch causes this structure to revert to a dihydride. In this process, sufficient energy is localized in the H–Ru–H bending mode to cross TS2, causing elimination at 800 fs.

Three elementary reaction steps that are common in homogeneous catalysis have been examined with path sampling to provide unique insights beyond that given by conventional quantum chemical calculations. Even at 300 K, the vibrational dynamics of this reaction have a significant effect on the molecular structure, how the rate-limiting barrier is crossed, and the elimination of the product. The localization of vibrational energy into H–Ru–H bending modes after the insertion step leads to rapid elimination of the ethane. As such, this mechanism is better understood as a concerted insertion–elimination mechanism with a transient Ru(IV) stage rather than a true stepwise mechanism, so observation of this Ru(IV) intermediate would require a spectroscopic technique operating on the subpicosecond time scale. This facile and direct cleavage of H<sub>2</sub> through a transient Ru(IV) dihydride intermediate may be of great value to the development of novel hydrogenation catalysts.

**Acknowledgment.** We thank NSERC and the Canada Research Chairs program for funding. We also thank Professor Deryn Fogg for thought-provoking discussions.

**Supporting Information Available:** Details of the calculations, MPG animation of a representative trajectory, histogram of intermediate lifetimes, Cartesian coordinates and electronic energies for structures in Figure 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA802219A